

Fundamental Research – Basics for Gas and Energy Saving Solutions Development

Bondarenko B.I., Karp I.N., Olabin V.M., Pyanyh K.Ye.
The Gas Institute of the National Academy of Sciences of Ukraine

One of the most crucial problems of Ukrainian economics is the considerable share of natural gas in fuel and energy balance, its high cost and dependence on import supplies. That is why research and developments of the Gas Institute of the National Academy of Sciences of Ukraine are aimed at improvement of solutions for gas application in industry and municipal engineering, along with total increase of energy efficiency of production. Plenty of energy saving solutions and equipment are offered at the world market. Creation of new solutions and considerable improvement of the existing ones can be implemented on the basis of fundamental research based on classic sciences - thermodynamics, heat transfer and gas dynamics. We call such research fundamental and purposeful.

Technical thermodynamics. The combined cycle of cold energy-t-work transformation in liquefied natural gas regasification units was offered. Its implementation will give a possibility to return a part of work, spent on liquefaction, for production of electrical energy in amount sufficient not only for satisfaction of own needs but also for energy supply to external customers.

The combined cycle of heat-to-work transformation was implemented at creation of highly efficient compressor station on one of the main gas pipelines of Ukraine.

Research of hydrocarbon systems thermodynamic equilibrium led to creation of a calculation program under the name of GazKondNeft. The program found a wide use at designing of gas processing plants. On its basis the process of hydrocarbon propellant production from Ukrainian raw material was developed and implemented. It gave a possibility to reject its import.

Chemical thermodynamics. Thermodynamic calculations of complex reactive systems are widely used at selection and improvement of metallurgical processes and solutions of natural gas replacement with alternative heat sources – coal, fuels of biological origin or technological gases. The calculation results were used in the development of industrial solutions, in particular, solutions of natural gas replacement with fuels with a less calorific potential.

The use of chemical equilibrium calculation methods gave the possibility to define limit compositions of generator gas and level of the gasification process derivation from equilibrium composition. On this basis, the reverse process of coal and biomass air gasification with maximal approach of generator gas composition to equilibrium composition was developed and implemented. Computerised thermodynamical simulation of reacting systems are often used as an instrument for assessment of thermodynamic perfection of processes. For calculations standard program “Terra” [1] is usually used.

Among fuels for natural gas substitution special place possesses biomass. The resources of biomass in Ukraine are estimated in more than twenty billions of equivalent quantity of natural gas. It is known, that natural gas in Ukrainian energy balance consists more than 50% among organic fuels. At the same time bigger part of it is imported on high prices. So, development of technologies and equipment for natural gas substitution by alternative fuels is in Ukraine very actual. It must be also mentioned, that biomass has unquestionable advantages in comparison with coal from the point of view of negative influence on environment and greenhouse effect.

The experimental and theoretic study of biomass gasification process was provided. A pilot batch-oriented gas generator for gasification of different biomass types was developed and tested (fig 1). The main task was to determine the heat characteristics of producer gas and to estimate possibilities of use it for natural gas substitution. The fundamentals used for the generator development were based upon technology by Sibtermo Company (Krasnoyarsk) applied for Kansk-

Achinsk brown coal gasification for semi-coke production purposes [3]. This technology uses inverse gasification process of very low productivity, so the approaching to chemical equilibrium must be maximal. The testing results are presented in Table 1 [4].

Table1. Gasification of solid fuels. Gas composition, substitution rates

| № p/p | Parameter | Solid fuels for gasification | | | | | |
|---|--|---------------------------------|----------------|-------------------|----------------|----------------|----------------|
| | | Wood chips (humidity 15%) | Rise husk | Pellets | | Lignite | Brown coal |
| | | | | Sunflower husk | Wood | | |
| The composition of the generator gas,% vol | | | | | | | |
| 1 | H ₂ | 13.35 | 11.36 | 16.86 | 11.3 | 12.24 | 20.01 |
| 2 | N ₂ | 48.83 | 54.8 | 44.92 | 49.45 | 55.24 | 49.27 |
| 3 | CO | 16.03 | 15.69 | 19.51 | 12.59 | 11.88 | 14.10 |
| 4 | CH ₄ | 5.57 | 4.72 | 5.81 | 6.71 | 4.24 | 3.32 |
| 5 | CO ₂ | 12.49 | 10.55 | 9.15 | 15.84 | 12.87 | 11.14 |
| 6 | C ₂ H ₄ | 0.77 | 0.55 | 0.71 | 0.95 | 0.98 | 0.13 |
| 7 | C ₂ H ₂ | 0.16 | 0.02 | 0.0 | 0.34 | 0.0 | 0.0 |
| 8 | C ₂ H ₆ | 0.11 | 0.07 | 0.18 | 0.21 | 0.0 | 0.11 |
| 9 | C ₃ H ₈ | 0.07 | 0.03 | 0.1 | 0.13 | 0.0 | 0.04 |
| 10 | H ₂ O | 2.62 | 2.21 | 2.69 | 2.49 | 2.34 | 1.88 |
| | Σ | 100 | 100 | 100 | 100 | 100 | 100 |
| Indicators of substitution and energy data | | | | | | | |
| 1 | Low calorific value, MJ/m ³ (kcal/m ³) | 6,13 (1464) | 5,24 (1251) | 6,97 (1664) | 6,77 (1617) | 4,92 (1175) | 5,32 (1270) |
| 2 | Solid fuels to replace 1 m ³ of natural gas, kg | 3.7 | 3.3 | 2.5 | 2.6 | 3.2 | 2.8 |

It is seen, that low calorific value of producer gas is at 1,7-1,8 times more than LCV of blast furnace gas and can be successfully used for natural gas substitution in low and middle temperature furnaces, boilers and gas engines. In high temperature processes both gas and air must be heated.

In parallels calculations of equilibrium content of producer gas, received by wood pellets gasification were provided. The results of its comparison with experimental content are given in Table 2.

Table 2. Comparison of calculated and experimental producer gas content

| Gas content | H ₂ | CO | CH ₄ | CmHn | N ₂ | CO ₂ | Residue (C _{solid} +ash) |
|------------------|----------------|-------|-----------------|------|----------------|-----------------|--------------------------------------|
| Calculated | 24,61 | 21,55 | 1,22 | 0,00 | 41,31 | 11,32 | 0,08 |
| Experimental (1) | 20,70 | 21,17 | 3,63 | 0,28 | 42,45 | 11,78 | 0,08 |
| Experimental (2) | 20,42 | 20,52 | 3,60 | 0,31 | 41,79 | 13,37 | 0,08 |

The difference between calculated and experimental results is not considerable. At the same time it shows imperfection of real process and points out the necessity and way of technology improvement.

Setting up of a complex with 1.8 MW installed capacity for wood pellets gasification is an example of the development and implementation of biomass gasification technology and equipment. The complex is designed for partial substitution of natural gas in the steam boiler heating system. It includes gas generator (fig. 2); gas purification and transportation system; dual fuel burner for simultaneous combustion of natural and producer gas; system of boiler operation

automatic support and the steam boiler. The complex has been operated at JSC "Malyn Paper Mill - Weidmann" (Malyn, Zhytomir region, Ukraine) since January 2011.

Significant thermal load fluctuations are specific to the company's technological process.

Average producer gas output, taking into account the power change, was 120 m³/hour in natural gas equivalent. The substitution of natural gas with producer gas did not result in the boiler productivity reduction. The development of an effective system for producer gas purification from resins and resin-containing items was an important result of this effort. The use of wood pellets for natural gas substitution enabled reduction of the costs for natural gas purchase by over 30%.



Fig1. The view of experimental gasification plant



Fig.2. The plant for biomass gasification of 1,8 MW capacity

Applied Theory of Combustion. The process of burn-out of biomass solid particles is an example of use of applied theory of combustion principles. Knowledge of biomass particles combustion parameters is needed for development of natural gas substitution in furnaces. The key parameter is time of burn-out of particle depending on its dimensions and humidity. This parameter determines possibility of use of definite kind biomass in heat apparatus. In process of development of furnace heating systems it must be also taken into consideration biofuel calorific value, conditions of ignition, ash melting temperature, flame position in furnace, formation of hazard wastes in a combustion process.

The burn-out of sawdust particles was investigated theoretically by mathematic model. The main stages of process were considered in sequence – free and bounded moisture removing, emission and combustion of volatile matters at particle surface, burn-out of coke residue. Model permitted to solve combined task of outer and internal heat exchange. The physical parameters of particle were taken into account – free volume of pores, its filling by free water, content of mineral and combustible parts of solid phase, part of volatile and bounded moisture. It was supposed, that particle is blown by oxygen content flow of constant temperature. The results of calculations are shown at fig.3 [5]. The curve at fig.5 shows that burning of coke residue defines particle burn-out time.

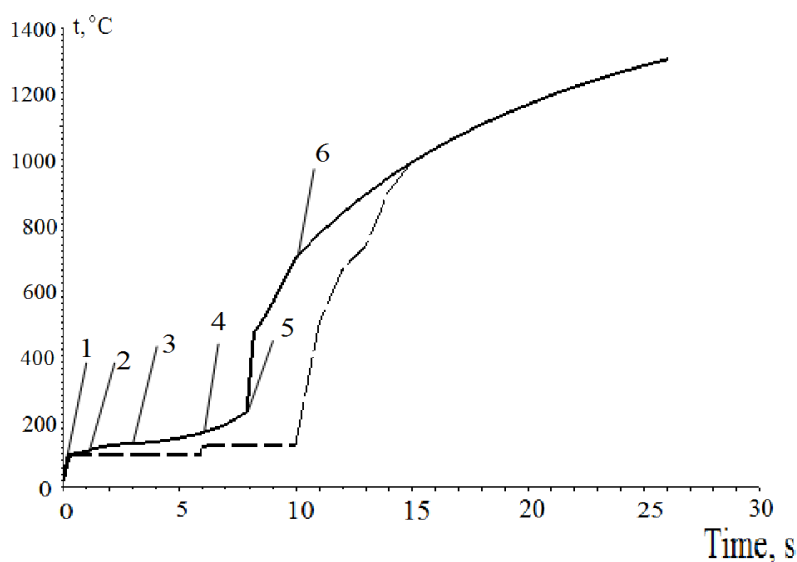


Fig.3. The temperature of center and surface of sawdust particle:

— - surface temperature; - - - - core temperature; in burn-out process:

1 - heating of particle to 100°C and free moisture removing beginning; 2 - removing of bounded moisture beginning; 3 – beginning of volatile matters emission; 4- end of free moisture removing; 5 – beginning of volatiles combustion at particle surface; 6 – complete volatiles combustion and beginning of coke residue combustion.

The time of the particles' combustion was experimentally determined on the installation of the fluidized bed with inert heat carrier during the combustion in the air at 900°C temperature. It follows from this experiment that wood waste burns out about two times quicker than the particles of sunflower husk. The deviation in the level of particles' moisture from the natural moisture (10-12%) results in the increases of their burnout time.

The results of the research are shown in Figure 4. The experimental data regarding the wood sawdust have coincided with the results of mathematical process modeling completely.

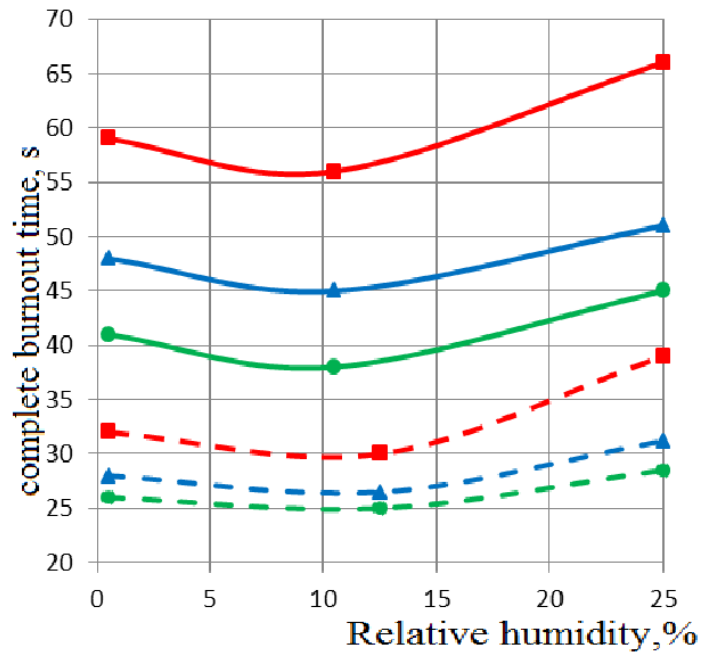


Fig.4. The dependence of sunflower husks and sawdust burn-out time on its diameter: ■ – 1,3 m; ▲ – 2,05 m; ● – 2,75 m; and humidity: ——— – husks; - - - - – sawdust.

The solution of using biofuel direct combustion technology was implemented on the rotary kiln of refractory clay firing at one Refractories in Ukraine. Technical re-equipment of the system was targeted at the maximum reduction of natural gas' usage through its substitution with pre-treated biofuel. The furnace specifications (fig5): 75 m length, 3.5 m diameter, 15 ton/hour output of final product. Average gas consumption before the project was 2200 m³/hour. Based upon the evaluation of the local biomass resources by the factory's experts, sunflower husk was selected as the principal biofuel, with the possibility to use waste wood (sawdust) as well. The task of shifting to the use of biomass presupposed the development of both technical requirements to the fuel, and technology of its co-combustion with natural gas.



Fig.5. Rotary kiln fueled by sunflower husk.

During the burning of mid-temperature fire-proof compounds the degree of natural gas substitution reached 70%, while in the process of burning of high-temperature fire-proof compounds - it was up to 50%.

The complex has been successfully operated since 2010. Annual volume of natural gas substitution with biofuel is over 10 million m³. The funds invested in the project had been repaid in less than 1 year.

Thermophysics, Heat and mass Transfer. The efficient method of heat and mass transfer intensification at high-temperature processing of mineral raw material by melting involves submerged combustion of gas and oxidant directly in the melting bath. Submerged combustion processes take place within complex hydrodynamic structure of bubbling melt.

Based on theoretical postulates set forth in paper [8] the conditions of stable ignition of fuel within the melt have been identified thus paving way to the development of submerged burners providing effective combustion of fuel-oxidant mixture within melt and uniform distribution of high-temperature combustion products over the entire volume of melting bath.

Heat exchange between high-temperature combustion products and particles of batch takes place through the melt. The analysis of heat exchange of the process peculiarities reveals that in the majority of cases combustion products - melt link in the entire process chain is the controlling factor.

The optimization of melting zone dimensions and geometrical configurations is a key approach to further perfection of bubbling bath type furnaces with submerged combustion in terms of their maximum thermal efficiency.

A relevant optimization technique has been developed to this end. A mathematical model of a solid amorphous particle melting in the bubbling silicate melt has been worked out and a computational algorithm of the formulated problem solution taking the approach characteristic of the integral method has been proposed [9]. The model adequacy is supported by good fit of computational experiment results and the experimental data obtained on a pilot melting furnace.

For successful practical application of the melting process involving submerged combustion of gas a new furnace design has been developed conceptually different from conventional units in that the melt in the melting bath is in a very agitated condition while more that a quarter of it being in a suspended state above the melt "surface" and the film of melt formed on the internal surfaces of the melting bath constantly moves. This state is generated by intensive bubbling that promotes dramatic rise in heat and mass transfer rates through expanded transfer surfaces. To prevent rapid wear of refractory lining the walls of submerged combustion melt tank are made of water-cooled panels protected by slag lining.

In spite of heat losses through the lining being around 30 - 60 kw/m² this drawback can be practically suppressed by rising furnace specific production capacity.

General view diagram of a bubbling bath type furnace with submerged combustion is shown in Fig. The field of effective application of the bubbling bath type furnaces is determined by the produced melt specific properties. The melt contains great quantity of entrapped gas in form of small bubbles which are not easily removable. The gas bubbles do not practically contain ingredients that can be subjected to thermal decomposition or sublimation. With this limitation in view the furnaces can be recommended for application in the technological processes that do not require melt clarification, specifically defluorination of ores,

desulphurization of slags, recovery of non-ferrous metals from slags by sublimation, processing of industrial or domestic waste.

Bubbling bath type furnaces proved their efficiency in the production of mineral wool for thermal insulation whose quality is not compromised by the presence of small gas bubbles in the melt. Apart from that these furnaces present much less environmental hazard as compared to the tank and shaft counterparts.

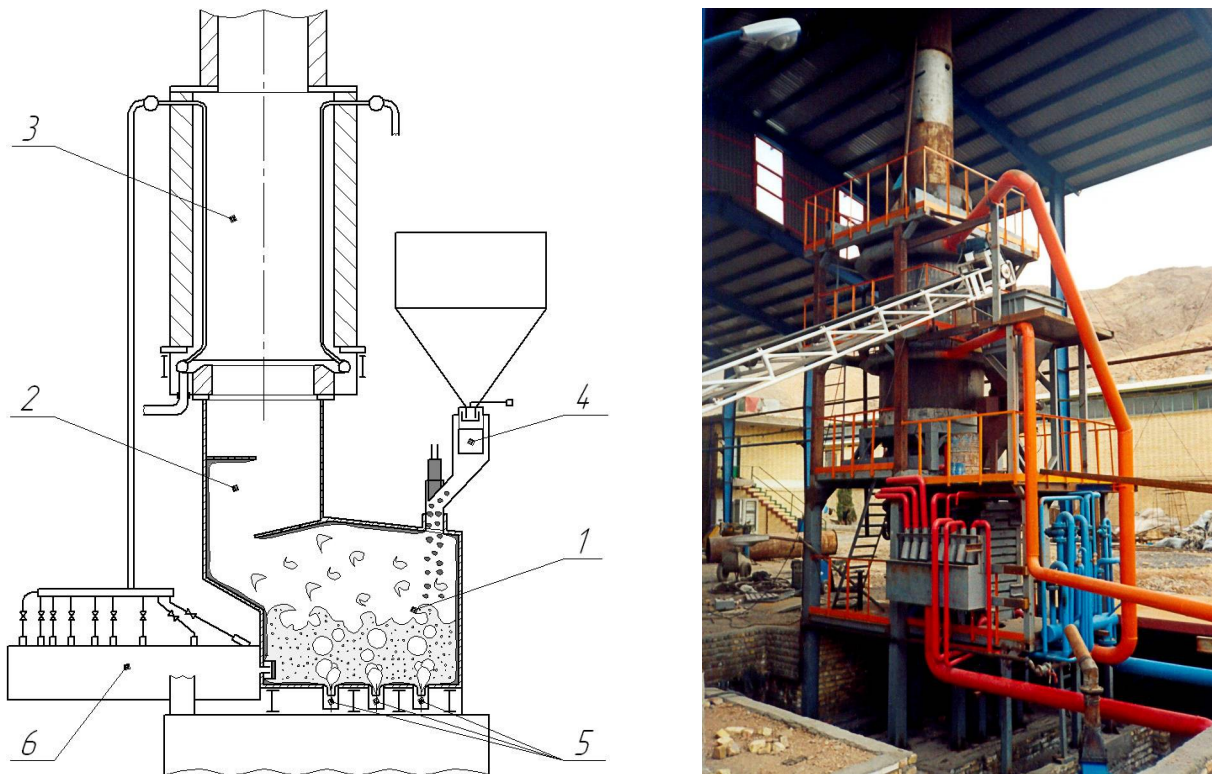


Fig.6. Bubbling bath type furnace
1. Melting bath; 2. Separation section; 3. Recuperator;
4. Charging device; 5. Submerged burners; 6. Heated channel

Plasma spraying. Thermal spraying is widely used as effective means of parts and pieces surface characteristics improvement. Among different technologies of thermal spraying plasma spraying is the most universal from the point of view of sprayed materials; the surface formed can satisfy to complex demands. Coating formed arise wear resistance, thermal stability, corrosion resistance of mashine elements. Effectiveness of plasma spraying process and coating quality depends on plasma working medium properties, in particular on its heat conduction. Heat flux from plasma flow to particles is directly proportional to thermal conductivity of working medium. Traditionally as working medium the mixture 75%Ar+25%H₂, rarely N₂ is used. In The Gas Institute of NASU we have investigated thermodynamic and transport properties of mixture of hydrocarbon gases - propane, methane, LPG - and air up to temperature 6000°C and have proposed on this basis to use it as medium for plasma spraying [9]. It was proved, that multicomponent chemically active

plasma of hydrocarbon gases — air mixtures has unique transport and thermal physical properties. From the technological point of view first of all they have 1) high thermal conductivity in wide temperature interval because of dissociation of almost all its components (fig.6), and 2) the possibility of oxidation- reduction potential of working medium control by changing gas:air relation. It is seen at fig.1, that curve of CH₄ –air mixture thermal conductivity has in contradistinction from other gases two peaks. So, heat flux has high meanings at all spraying distance. Economical and operational advantages of gas-air plasma usage in comparison with traditional working mediums are also obvious. Accessibility and cheapness of plasma of hydrocarbon gases — air mixtures makes its use preferable with plants power increasing and especially in supersonic plasma torches, when gas consumption arises dramatically. The usage of hydrocarbon gases — air mixtures as working medium for plasma spraying permits to create coatings of extremely high quality and sometimes by materials, which could not be sprayed by other technologies.

For realization of the technical ideology of thermal spraying by hydrocarbons-air plasma the equipment was developed and widely implemented by The Gas Institute and The Welding Institute of NAS of Ukraine in cooperation with other companies. The range of supersonic plasma torches and apparatus complexes for hydrocarbons-air plasma of 40, 80 and 160 kW are developed. At the same time the technologies of thermal spraying were developed, taking into account the peculiarities of plasma.

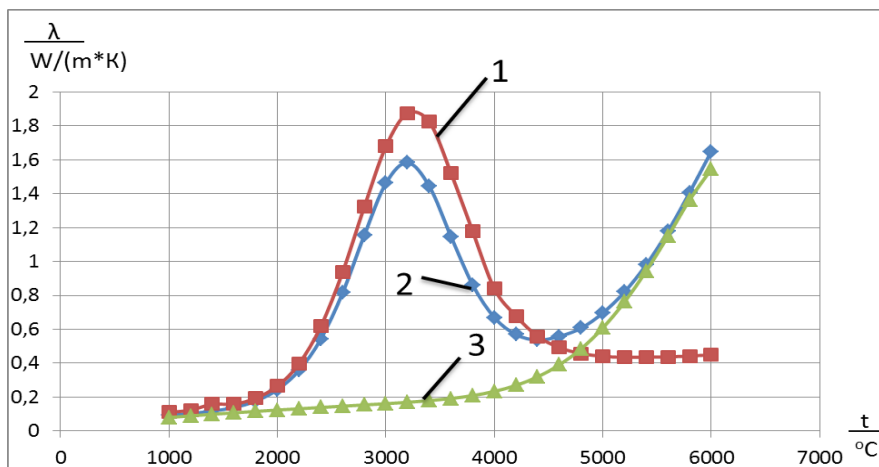


Fig. 7. Dependence of thermal conductivity on temperature for different gases:
 1 – 75%Ar+25% H₂; 2 – CH₄-air stoichiometric mixture; 3 – N₂.

High productive supersonic plasma spraying corrosion resistive coatings is used for technological pipelines protection since year 1995. Technology and semi-automatic machine for axis multiple-wear wheel restoration is successfully implemented at the repair factory. Supersonic plasma spraying and specially developed for this purpose semi-automatic machine are implemented for internal surfaces of powerful diesel engines sleeves of cylinders coating. The process of spraying is shown at fig.7.

Technologies and equipment described can be undoubtedly considered as high-tech. They have

promising future for being implemented at different enterprises worldwide.



Fig. 8. The process of plasma spraying of thermal barrier coating on the part of the pyrolysis reactor.

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